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(56) Documents Cited

EP 0078120 A1

US 4751273 A

US 4577205 A

US 4138255 A

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(54) **Printing process**

(57) A process of forming printed indicia upon a substrate, the substrate being intended to be brought into contact with a foodstuff, comprises forming patterned indicia upon the substrate of a composition comprising: (i) one or more ethylenically unsaturated monomers; and (ii) a polyether-containing compound; and curing the applied indicia by exposure to a beam of electrons. This renders the indicia inert, and should prevent taint or odour from effecting the foodstuff.

GB 2 284 787

PRINTING PROCESS

This invention is concerned with improvements in and relating to printing and, more particularly, to the printing of materials, such as printed packaging or wrapping materials, intended for the packaging of foodstuffs and whose printed indicia (or components therefrom) may come into indirect contact with the foodstuff.

Foodstuffs are commonly packaged in a wrapping or packing formed of synthetic plastics materials such as polyethylene, polypropylene, polyesters, or polyamides, or combinations of these with other packaging materials such as paper, board and/or metal foil. It is frequently desired to print upon such packaging to provide labelling, information, decoration, etc. Since the printed indicia (or components therefrom) may come into contact with the foodstuff it is most desirable that the printed indicia be as inert as possible to the foodstuff and that no components from the printed indicia be extracted or migrate into the foodstuff. Such migration or extractable components are undesirable as there is the strong possibility that they may impart taint or odour to the packaged foodstuff.

It has now been found, in accordance with the present invention, that printed indicia having remarkably low contents of extractable components may be produced by the electron beam curing of certain compositions, as hereinafter more particularly defined, containing ethylenically unsaturated components and an ether component.

According to the invention, therefore, there is provided a process of forming printed indicia upon a substrate intended as a packaging material for foodstuffs, which process comprises forming patterned indicia upon the substrate of a composition comprising:

- (i) one or more ethylenically unsaturated monomers;
and
- (ii) a polyether-containing compound;

and curing the applied indicia by exposure to ionising radiation (e.g. nuclear radiation, pile radiation, α or β -radiation and, especially, a beam of electrons).

The principal polymerisable (curable) portion of the composition used in accordance with the invention comprises one or more ethylenically unsaturated monomers, preferably one or more polyethylenically

unsaturated (meth)acrylate monomers, that is acrylic or methacrylic acid esters of alcohols, especially aliphatic alcohols, containing two or more hydroxyl groups. Specific examples of such poly(meth)acrylate monomers include propoxylated glycerol triacrylate (GPTA), trimethylpropane triacrylate (TMPTA), tripropylene glycol triacrylate (TPGDA) and hexanediol diacrylate (HDDA). Other ethylenically unsaturated monomers which may be used include vinyl monomers such as N-vinyl pyrrolidone. The ethylenically unsaturated component of the composition is suitably present in the composition in an amount of from 0.1 to 90% by weight, preferably from 10 to 80% by weight, based on the total amount of components (i) and (ii).

The polyether-containing compound is suitably one containing repeating units of the formula:-

- RO -

in which R is a straight or branched C_1-C_4 alkylene group.

The polyether-containing compound may suitably be a polyalkylene glycol, such as polyethylene glycol (PEG), polypropyleneglycol (PPG) or polytetramethyleneglycol, which glycol may further be esterified or etherified. In accordance with a preferred feature of the invention

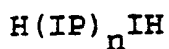
the polyether grouping is linked to an ethylenically unsaturated group. This is conveniently achieved by reacting a polyether glycol with a urethane acrylate, that is the reaction product of a polyisocyanate and a hydroxyl group-containing (meth)acrylate.

The urethane acrylate component is generally the simple reaction product of an acrylate functional alcohol, preferably containing one hydroxyl group and one or more ethylenically unsaturated groups, e.g. a hydroxyalkyl (meth)acrylate, with an aliphatic polyisocyanate, especially an aliphatic diisocyanate such as, for example isophorone diisocyanate (IPDI), tetramethylxylene diisocyanate (TMXDI), hexamethylene diisocyanate (HMDI), bis-(4,4'-isocyanato-cyclohexyl)-methane (H_{12} MDI, Desmodur W), 2,2,4-trimethylhexamethylene diisocyanate (TMDI) and derivatives thereof such as the biuret trimer of HMDI (Desmodur N3200). The polyether component is suitably a polyalkyleneoxy ether or derivative thereof, such as a polyethylene glycol or polypropylene glycol or polytetramethylene glycol, suitably having a molecular weight in the range 100 to 10,000, preferably 650 to 2000.

The combined urethane acrylate polyether species is preferably the reaction product of an aliphatic polyisocyanate (e.g. an aliphatic diisocyanate as noted above), a polyether polyol (e.g. polyethylene glycol or

polypropylene glycol as noted above) and a hydroxyalkyl (meth)acrylate. In accordance with one procedure the polyisocyanate and diol are first reacted together, using a stiochoimetric excess of isocyanate, to provide an isocyanate group-containing oligomer which is subsequently reacted with the hydroxyalkyl (meth)acrylate. In an alternative procedure the diisocyanate and hydroxyalkyl (meth)acrylate are first reacted together in equimolar proportions and the resultant product then reacted with the polyalkylene glycol.

One particular class of oligomers comprises those derived from the reaction of an aliphatic diisocyanate with a polyetherdiol and a hydroxyalkyl acrylate and which may be represented by the illustrative formula:



in which H represents the residue of a hydroxyalkyl acrylate group, I represents the residue of an aliphatic diisocyanate, P represents the residue of a polyether diol and n is an integer from 1 to 20, preferably from 1 to 5.

The polyether component preferably forms from 0.1 to 90% by weight of the total composition, more especially 5 to 60% by weight thereof.

In addition to the basic components (i) and (ii), the compositions used in the process of the invention can, and most usually will, contain other ingredients, especially colourants such as dyestuffs or pigments. These should be present in amounts sufficient to afford the desired level of colouration to the cured composition, e.g. in amounts of upto 10% by weight in the case of dyestuffs and amounts of up to 60% by weight in the case of pigments, preferably 5-30% by weight. Other components which may be present in the compositions include fillers and extenders and waxes, silicone surfactants, rheology modifiers, stabilisers, adhesion promoters and slip agents. Such other components are discussed in more detail in "The Printing Ink Manual", 5th Edition, Leach & Pierce (Eds), Blueprint 1993, especially at Chapter 4.

The composition used in accordance with the invention is printed onto the substrate by any suitable process such as offset lithography, dry offset, letterpress, flexography, rotogravure, screen printing, roller printing, spray coating, dip coating and curtain coating. After having been printed upon the substrate, the indicia should, of course, be cured and this is affected, in accordance with the invention, by ionising radiation e.g. by exposure to an electron beam. The exposure dose will generally be such as is conventionally used for electron beam curing of printed

indicia, e.g. 0.1 to 10 Mrad, preferably 1-3 Mrad, and will suitably be carried out in an atmosphere of reduced oxygen content, e.g. having less than 100 ppm of oxygen.

In order that the invention may be well understood the following Examples are given by way of illustration only.

Preparative Example I (INTERMEDIATE I)

222g Isophorone diisocyanate (1 mole) and 0.3g (1000 ppm) 2,6-di-t-butyl-4-methylphenol (BHT) were placed in a four-necked, glass reaction vessel equipped with a stirrer, thermostat, thermometer, reflux condenser and air sparge. This was heated to 40°C, then 0.1g (300 ppm) of dibutyltin dilaurate catalyst was added. 104.4g of 2-hydroxy ethyl acrylate (0.9 mole) were added slowly over 1 1/2 hours, the temperature being allowed to rise to 50-60°C at the end of the addition. The reaction was continued for three hours when the isocyanate value was determined to be 3.49×10^3 eq/g (theoretical value 3.37×10^3 eq/g). Intermediate I (326.4g) is obtained as a low viscosity clear liquid.

EXAMPLE 1

85.0g (0.297 eq.) of intermediate I (was charged into the reaction vessel, together with 0.1g (1000 ppm) dibutyl tin dilaurate. The mixture was heated to 40°C and 34.5g hydroxyethyl acrylate (0.297 mole) was added over two hours. The reaction mixture was held at 60°C for 7 hours until there was no isocyanate remaining as determined by infrared spectroscopy. Oligomer I (117.8g) was obtained as a clear, highly viscous liquid.

EXAMPLE 2

110.3g (0.385 eq.NCO) of intermediate I, 0.1g dibutyl tin dilaurate (300 ppm) and 0.1g (300 ppm) 2,6-ditertiarybutyl-4-methylphenol were charged into a reaction vessel and heated to 40°C under air sparge. 200g (0.390 eq.OH) of polypropylene glycol (MW 1000) were slowly added over two hours. At the end of the addition, the temperature was raised to 60°C and held for 3.5 hours, until no isocyanate peak was visible by infrared spectroscopy. Oligomer II (310g) was obtained as a clear, water white viscous liquid.

EXAMPLE 3

Intermediate I was prepared as described above having an isocyanate value of 3.27×10^3 eq.NCO/g.

80g of this intermediate I (0.262 eq.) was charged into the reaction vessel together with 0.075g (200 ppm) 2,6-di-t-butyl-4-methylphenol and 0.075g (200 ppm) dibutyl tin dilaurate, and the mixture heated to 50°C. 93.5g (0.522 OH equivalents) of glycerol monostearate was added slowly and reacted until no isocyanate remained. IPDI (60g, 0.540 NCO eq.) was added and the reaction continued at 60°C until the isocyanate value had decreased to 1.42×10^{-3} eq. NCO/g. 143.5g (0.280 eq. OH) of PPG 1000 was slowly added and the reaction continued until no isocyanate peak was detectable by infrared spectroscopy. Oligomer III was obtained as a highly viscous, amber liquid.

COATINGS PREPARATION

Coatings of the above oligomers were prepared along with comparative oligomers, to investigate EB curing properties.

Ingredient	Coatings	I	II	III	IV	V	VI
Oligomer I		50	-	-	-	-	18.2
Oligomer II		-	50	-	-	-	-
Oligomer III		-	-	50	-	-	-
Urethane acrylate ¹⁾		-	-	-	50	-	-
Epoxy acrylate ²⁾		-	-	-	-	50	-
PPG 1025		-	-	-	-	-	31.8
GPTA ³⁾		50	50	50	50	50	50
		100g	100g	100g	100g	100g	100.0g

Where necessary, the mixtures were heated gently at 60°C to aid dissolution of the oligomer in the monomer.

i) A commercially available polyester urethane acrylate.

ii) A commercially available Bisphenol A epoxy acrylate.

iii) A commercially available propoxylated glycerol triacrylate.

Coating	Dose/Mrad	Extractable GPTA/ppm
I	3	11,500
II	3	45
III	3	65
IV	3	900
V	3	15,830
VI	3	400

APPLICATION AND CURING

Coatings were applied using a No. 1 K-bar (notional wet film weight 10 g/m^2) onto corona treated LDPE (Brithene BLA). The prints were exposed to varying doses of electron beam radiation using an ESI Electrocurtain LB80 curing unit. All films were exposed in an atmosphere containing < 100 ppm oxygen.

EXTRACTION

The quantity of unreacted monomer (GPTA) in the films was determined using solvent extraction. A known quantity of coating is subjected to a 16 hour cold soaking in dichloromethane.

The extract is concentrated, an internal standard

assayed using a gas chromatograph with a mass selective detector (gc/ms).

The quantity of extractable GPTA is expressed as a fraction of the original coating weight and is quoted in ppm.

Example 4

A polyether urethane (Intermediate II) was prepared by reacting 185.92g of Desmodur N3300 (an isocyanurate trimer of HMDI, NCO content = 21.5%) with a blend of 293.14g of Bisomer PPA6E (a hexapropylene glycol-monoacrylate ex International Speciality Chemicals) and 120.04g of Tone M0100 (an oligocaprolactone monoacrylate ex Union Carbide) in the presence of 0.6g BHT and 0.3g dibutyl tin dilaurate. The reaction was carried out in the same manner as the previous examples and continued until no isocyanate peak was visible by infra-red spectroscopy.

Intermediate II was obtained as a low viscosity, clear liquid.

Preparation of Offset Inks (Coatings VII and VIII)

Offset inks were prepared according to the following formulae

	<u>Coating VII</u>	<u>Coating VIII</u>
Phthalocyanine blue pigment	20.00	20.00
Calcium carbonate	3.00	3.00
Talc	2.40	2.40
Intermediate II	54.64	-
Polyester oligomer*	-	55.25
GPTA	19.20	18.59
Stabiliser	0.76	0.76
	<hr/>	<hr/>
	<u>100.00</u>	<u>100.00</u>

*A commercially available polyester hexacrylate.

The inks were prepared by grinding the pigment, calcium carbonate and talc into the other ingredients using a three-roll mill.

Inks were printed at a film weight of 1.9-2.0g/m² onto Melinex O (polyethylene terephthalate film) and cured using an electron beam pilot line with a dose of 3Mrad and <100ppm of oxygen.

The cured films were then extracted and assayed for residual GPTA as previously described.

Results

	<u>Dose/Mrad</u>	Extractable <u>GPTA/ppm</u>	%GPTA <u>converted</u>
Coating VII	3	8,140	95.7
Coating VIII	3	29,760	84.0

* = $[1 - (\text{extractable GPTA} / \text{GPTA loading in ink}) \times 100\%$

CLAIMS:

1. A process of forming printed indicia upon a substrate, the substrate being intended to be brought into contact with a foodstuff, which process comprises forming patterned indicia upon the substrate of a composition comprising:

- (i) one or more ethylenically unsaturated monomers; and
- (ii) an polyether-containing compound;

and curing the applied indicia by exposure to a beam of electrons.

2. A process as claimed in claim 1 in which the polyether-containing compound is also ethylenically unsaturated.

3. A process as claimed in claim 2 in which the polyether-containing compound is the reaction product of an aliphatic polyisocyanate, polyether diol and hydroxyalkyl (meth)acrylate.

4. A method as claimed in claim 1 substantially as hereinbefore with reference to the Examples.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

Application number
 GB 9325574.3

Relevant Technical Fields

- (i) UK Cl (Ed.M) B6C: CBQB
- (ii) Int Cl (Ed.5) B41F: 23/04

Search Examiner
 A DAVEY

Date of completion of Search
 3 FEBRUARY 1994

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASE: WPI

Documents considered relevant following a search in respect of Claims :-
 1-4

Categories of documents

- X:** Document indicating lack of novelty or of inventive step.
- Y:** Document indicating lack of inventive step if combined with one or more other documents of the same category.
- A:** Document indicating technological background and/or state of the art.
- P:** Document published on or after the declared priority date but before the filing date of the present application.
- E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.
- &:** Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
X	EP 0078120 A (ALBUM) see eg page 11 line 9	1
X	US 4751273 (ALLIED SIGNAL) whole document	1
X	US 4577205 (RICOH) whole document	1
X	US 4138255 (GENERAL ELECTRIC) whole document	1
	WPI Accession Numbers 92-012109/02 and JP 3261555 (TORAY) (see abstract)	1

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents)

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